

Optical properties of aligned carbon nanotube mats for photonic applications

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We studied the optical properties of the aligned carbon nanotube (16, 0), (10, 0), and (8, 4) mats for photonic device applications. We employed *ab initio* density functional potentials and utilized the linear combination of atomic orbital formalism. We calculated the electronic structure of the carbon nanotube mats and the real and imaginary parts of the dielectric functions as functions of the photon energy. The calculated dielectric functions of the aligned carbon nanotube mats show a strong anisotropy when the electric field of the light is parallel or perpendicular to the tube axes. Especially, there are strong peaks in the imaginary part of the dielectric function near the absorption edges, when the electric field of the light is parallel to the carbon nanotube axes. The unusual optical properties of the semiconducting carbon nanotube mats present an opportunity for applications in electro-optical devices in the infrared energy region. © 2006 American Institute of Physics.

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I. INTRODUCTION

Carbon nanotubes possess unique electronic properties that are very useful for building electro-optical devices at nanometer scales. Recently, Wu *et al.* reported ultrathin, transparent, optically homogeneous, electrically conducting films of pure single-walled carbon nanotubes.¹ The films exhibit optical transmittance comparable to that of commercial indium tin oxide in the visible spectrum, but far superior transmittance in the technologically relevant 2–5 μm infrared spectral band. These characteristics indicate broad applicability of the films for electrical coupling in photonic devices. Kim *et al.* reported highly polarized absorption and photoluminescence of stretch-aligned single-walled carbon nanotubes dispersed in gelatin films.² The highly polarized absorption and photoluminescence are attributed to interband optical transitions in the single-walled carbon nanotubes (SWCNTs). The realization of highly aligned and luminescent SWCNT thin films should contribute to the development of SWCNTs as optoelectronic materials. Li *et al.* also reported polarized optical absorption spectra of single-walled 4 Å carbon nanotubes arrayed in the channels of an AlPO₄-5 single crystal.³ The measured absorption spectra agreed well with the *ab initio* calculations based on the local density functional approximation. Carbon nanotubes may also be used in optical limiting, nonlinear optical devices, and other applications^{4–10}

Guo *et al.* reported the linear and nonlinear optical properties of individual carbon nanotubes, utilizing full-potential projected augmented wave (PAW) method.¹¹ The calculations were based on *ab initio* density functional calculation within the local density functional approximation (LDA). A

supercell geometry was adopted so that the nanotubes are aligned in a square array with the closest distance between adjacent nanotubes being at least 6 Å. They performed test calculations with larger intertube distances and no discernable differences were found. In their work, they aimed to study the optical properties of isolated or nearly isolated carbon nanotubes.

Machon *et al.* performed *ab initio* density functional calculations for the optical properties of 4 Å diameter single-walled carbon nanotubes.¹² The calculated optical properties confirmed the experimental results of Li *et al.*³ for the strong anisotropy of the optical response of carbon nanotubes.

In optoelectronic applications, a large number of carbon nanotubes will be assembled in a desired form. As identified in the experimental studies, single-walled carbon nanotubes are self-assembled in a triangular lattice in bundles, strands, or mats.^{13,14} The photonic devices based on carbon nanotubes can take advantage of the strong anisotropy of optical properties of SWCNTs under polarized light. This can be achieved by aligning the SWCNTs in a certain direction to form carbon nanotube mats. In this work, we aimed to study the optical properties of aligned carbon nanotube mats (CNTMs), using *ab initio* density functional calculations. We utilized the computational method of the linear combination of atomic orbital (LCAO) formalism. We calculated the optical properties of various CNTMs that were constructed from semiconducting SWCNTs. As a further pursuit of the applications of nanodevices, we demonstrate in this work that the aligned carbon nanotube mats will have relevant properties for photonic applications.

II. METHOD

We performed *ab initio* quantum calculations that are based on the density functional theory of Hohenberg-Kohn

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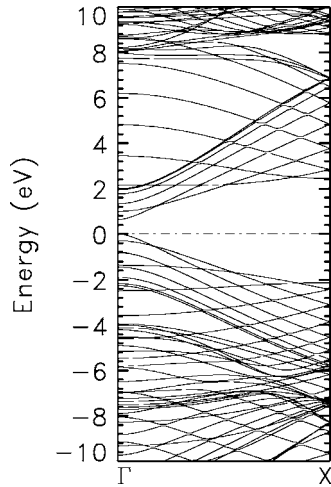


FIG. 1. The electron energy bands of SWCNT (16, 0).

and Kohn-Sham.^{15–19} The many-body exchange and correlation interactions of the electron gas are described by the density functional potential in a local density approximation (LDA). We used the Ceperley-Alder form of the exchange-correlation potential.²⁰ As we reported in the previous publications on the calculations of the electronic structure of SWCNTs,¹⁶ we also performed *ab initio* calculations using the generalized gradient approximation (GGA) potential of Perdew and Yue.²¹ We compared the electron energy bands of the SWCNTs from the LDA and GGA calculations. The average difference between the energy bands, resulting from the two potentials, was about 1 mRy. We utilized the LCAO method in solving the Kohn-Sham equations.^{22,23} We employed an extended basis set that includes atomic orbitals of C(1s2s3s 2p3p). Here C(3s 3p) are the extra orbitals that are used to augment the basis set to account for possible charge diffusion and polarization in the CNTMs. The real space approach of the LCAO method enables us to complete the required large-scale computations using our Silicon-Graphics Origin2000 that is equipped with 2 GB random access memory (RAM).

As identified in the experimental studies, single-walled carbon nanotubes are self-assembled in a triangular lattice in bundles, strands, or mats. We constructed the carbon nanotube mats by aligning the SWCNTs in an array of the triangular lattice. We vary the distances between the SWCNTs to simulate the different samples of the interactions in the mats. We performed *ab initio* density functional calculations to study the electronic structure of the aligned carbon nanotube mats. We also carried out *ab initio* total energy calculations for the carbon nanotube mats at various tube-tube distances.

For the studies of the optical properties of the aligned CNTMs for photonic applications, we are particularly interested in the semiconducting SWCNTs. We utilized the calculated electronic energy levels and related wave functions to evaluate the dielectric function of the aligned CNTMs. We calculated the real and imaginary parts of the dielectric function of CNTMs as functions of photon energies. The imaginary part of the dielectric function $\epsilon_2(\omega)$, from the direct interband transitions, is calculated from the Kubo-Greenwood formula,²⁴

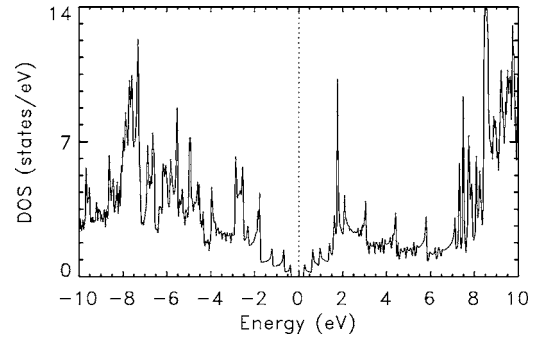


FIG. 2. The electron density of states of SWCNT (16, 0).

$$\epsilon_2(\omega) = \frac{8\pi^2 e^2}{3m_e^2 \hbar \omega^2 \Omega} \sum_{\mathbf{k}} \sum_{nl} |\langle \Psi_{\mathbf{k}n}(\mathbf{r}) | \mathbf{P} | \Psi_{\mathbf{k}l}(\mathbf{r}) \rangle|^2 f_{\mathbf{k}l} (1 - f_{\mathbf{k}n}) \times \delta(\epsilon_{\mathbf{k}n} - \epsilon_{\mathbf{k}l} - \hbar\omega), \quad (1)$$

where $\hbar\omega$ is the photon energy; \mathbf{P} is the momentum operator, $\mathbf{P} = -i\hbar\nabla$; $\epsilon_{\mathbf{k}l}$ and $\Psi_{\mathbf{k}l}$ are the eigenenergy and related eigen-wave function of the l th state at \mathbf{k} point in the Brillouin zone; $f_{\mathbf{k}l}$ is the Fermi distribution function; and Ω is the volume of the triangular lattice unit cell. The real part of the dielectric function $\epsilon_1(\omega)$ was found from the well-known Kramers-Kronig (K-K) relation.

III. RESULTS

A. Single-walled carbon nanotube (16, 0) mat

We constructed the carbon nanotube mat utilizing SWCNT (16, 0) as the basic building block. The diameter of individual SWCNT (16, 0) is 1.25 nm, which is comparable to the ones that were experimentally studied by Kazaoui *et al.*²⁵

We calculated the electronic structure of individual SWCNT (16, 0). There are 64 atoms in the tube unit cell of SWCNT (16, 0). The large number of atoms per unit cell that enter into the *ab initio* calculations presents some technical challenges. We utilized a real space approach of LCAO calculations. The calculated electron energy bands of SWCNT (16, 0) are presented in Fig. 1, where $\Gamma = (0, 0, 0)$, $Z = \pi/T(0, 0, 1)$, and T is the length of the tube unit cell. Figure 1 shows a direct band gap of 0.62 eV at the Γ point. The calculated density of states (DOS) of SWCNT (16, 0) is shown in Fig. 2. The van Hove singularities at the band edges and the sharp structures in the density of states are attributed to the one-dimensional (1D) tube structure.

Subsequently, we calculated the electronic structure of the carbon nanotube mat. In contrast to the work of Guo *et al.*,¹¹ we aligned the SWCNTs (16, 0) in a triangular lattice to form the mat. Guo *et al.* used a supercell geometry, and the nanotubes were aligned in a square array with the closest distance between the adjacent nanotubes being at least 6 Å. In this work, we performed the *ab initio* total energy calculations for the carbon nanotube mats at various tube-tube distances. The total energy minimization found the stable tube-tube distance at 3.5 Å, which is close to the interplanar distance (3.35 Å) of graphite.

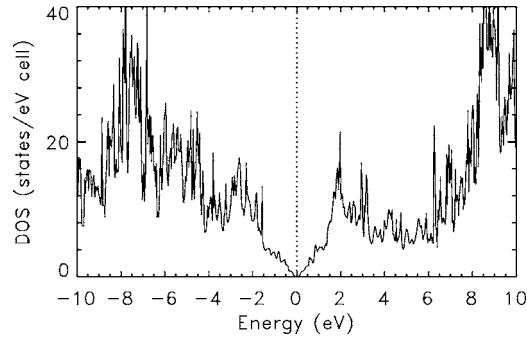


FIG. 3. The electron density of states of carbon nanotube (16, 0) mat at the tube-tube distance of 3.5 Å.

In Fig. 3, we present the electron density of states of the carbon nanotube mat, which was constructed from SWCNTs (16, 0) and the tube-tube distance was at 3.5 Å. The density of states of the CNTM in Fig. 3 retained the van Hove singularities. The weak interaction between the nanotubes slightly smeared the sharp peak structures in the DOS as compared to those of SWCNTs in Fig. 2.

Utilizing the electron energy levels and related wave functions from the electronic structure computations, we further calculated the optical properties of the carbon nanotube mat. We calculated the imaginary (ϵ_2) part of the dielectric function as a function of photon energy. The real part of the dielectric function $\epsilon_1(\omega)$ was found from the K-K relation. The calculated dielectric function revealed a strong anisotropy when the electric field (E) of the light is parallel or perpendicular to the tube axis. We present, in Fig. 4, the

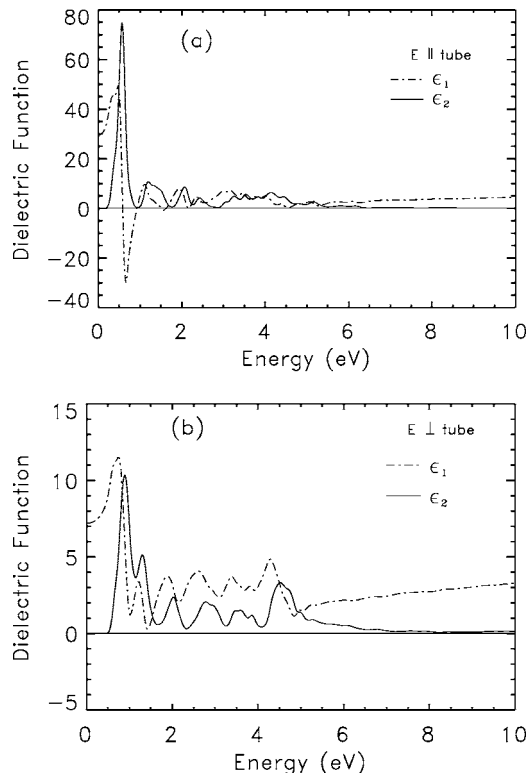


FIG. 4. The calculated real and imaginary parts of the dielectric function, $\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$, of the carbon nanotube (16, 0) mat which has the tube-tube distance of 3.5 Å between the SWCNTs (16, 0).

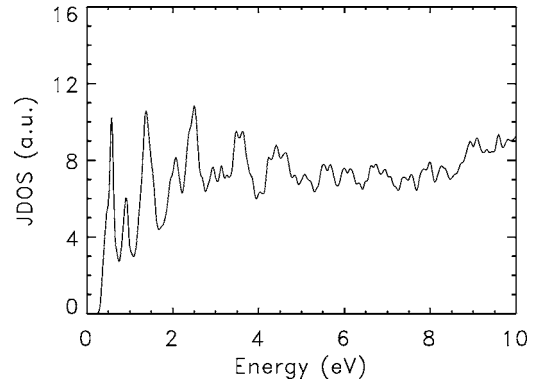


FIG. 5. The joint density of states for the aligned carbon nanotube (16, 0) mat.

calculated dielectric function of the aligned nanotube mat, for the tube-tube distance of 3.5 Å between the individual SWCNTs (16, 0). Figures 4(a) and 4(b) present the dielectric functions (ϵ_1, ϵ_2) for the electric field of the light parallel and perpendicular to the tube axis, respectively. When the electric field of the light is parallel to the tube axis, the imaginary part of the dielectric function ϵ_2 has a strong peak at the photon energy of about 0.58 eV, as in Fig. 4(a). The height of the first peak of ϵ_2 in Fig. 4(a) can reach a value of about 60, which is about a factor of 7 higher than that of the first peak of ϵ_2 (at 0.9 eV) in Fig. 4(b). The strong peak in ϵ_2 in the low photon energy region in Fig. 4(a) shows a strong anisotropy in the optical properties of CNTM and is spectacularly different from that of conventional optical materials. The above strong peak in ϵ_2 indicates that the carbon nanotube mats can be used as photonic sensors in the infrared region. Such unusual optical properties in semiconducting carbon nanotube mats present an opportunity for applications in electro-optical devices.

We further studied the physical factors for the strong anisotropy in the optical properties of the aligned carbon nanotube mat. Particularly, a strong anisotropy is observed in the first peaks of the imaginary parts of the dielectric function when the polarization of the light is parallel or perpendicular to the tube axis. It is noted that the first absorption peak in ϵ_2 , in the aligned CNTM, is associated with the van Hove singularities that are located just above and below the Fermi level. We calculated a joint density of states (JDOS) that is based on the same calculation formula as that of the computation of ϵ_2 , but without the inclusion of the electron excitation matrix elements in the calculation. The calculated JDOS of the aligned carbon nanotube (16, 0) mat is shown in Fig. 5. The first peak of the JDOS in Fig. 5, at 0.58 eV, is associated with the first peak of ϵ_2 in Fig. 4(a) when the electric field of the light is parallel to the tube axis. The second peak of the JDOS in Fig. 5, at about 0.9 eV, is associated with the first peak of ϵ_2 in Fig. 4(b) when the electric field of the light is perpendicular to the tube axis. The height of the first peak of the JDOS in Fig. 5 is greater than that of the second peak, with a ratio of 1.67. The electron excitation matrix elements that contribute to the first peak of ϵ_2 in Fig. 4(a) have a much higher value than those contributing to the first peak of ϵ_2 in Fig. 4(b). The ratio of the excitation matrix

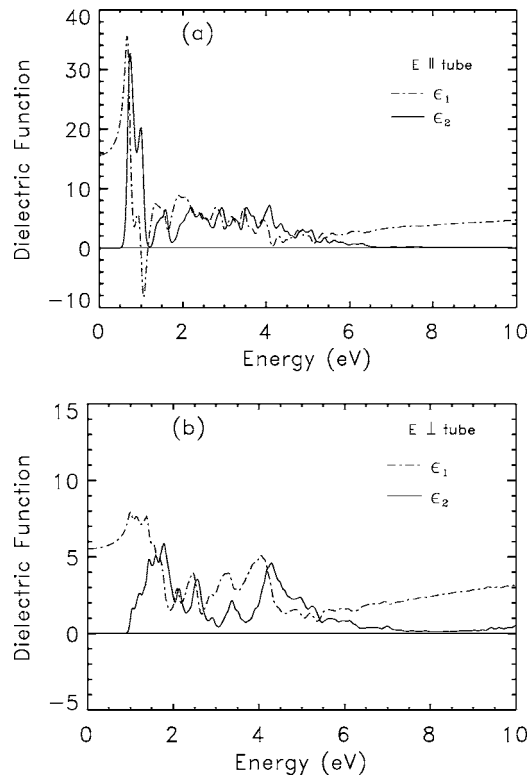


FIG. 6. The calculated real and imaginary parts of the dielectric function of the carbon nanotube (10, 0) mat which has the tube-tube distance of 3.34 Å between the individual SWCNTs (10, 0).

elements accounting for these two peaks is about 4–5. Hence, the strong anisotropy in ϵ_2 is mainly attributed to the electron excitation matrix elements when the polarization of the light is in different directions.

B. Single-walled carbon nanotube (10, 0) mat

The electronic structure of individual SWCNT (10, 0), from *ab initio* density functional calculations, was presented in previous publications.^{16,26} The diameter of individual SWCNT (10, 0) is 7.83 Å. In this work, we calculated the optical properties of the aligned carbon nanotube (10, 0) mat for electro-optical device applications. The SWCNTs (10, 0) are arranged in a triangular lattice in the aligned CNTM. We performed *ab initio* electronic structure calculations for the aligned carbon nanotube (10, 0) mats. We employed the *ab initio* total energy minimization that found a stable tube-tube distance at 3.34 Å. In Fig. 6, we present the calculated real and imaginary parts of the dielectric function of the carbon nanotube (10, 0) mat, for the tube-tube distance of 3.34 Å. The general feature of the dielectric function of the aligned carbon nanotube (10, 0) mat is similar to that of the (16, 0) mat. The calculated imaginary parts of the dielectric function in Fig. 6(a), for the electric field of the light parallel to the tube axis, shows a strong peak near the absorption edge at about 0.75 eV. When the electric field of the light is perpendicular to the tube axis, the absorption is much weaker, as shown in Fig. 6(b). This feature again presents a strong anisotropy in the optical properties of the aligned carbon nanotube (10, 0) mat. The height of the first peak in ϵ_2 in Fig. 6(a) for the carbon nanotube (10, 0) mat is lower than

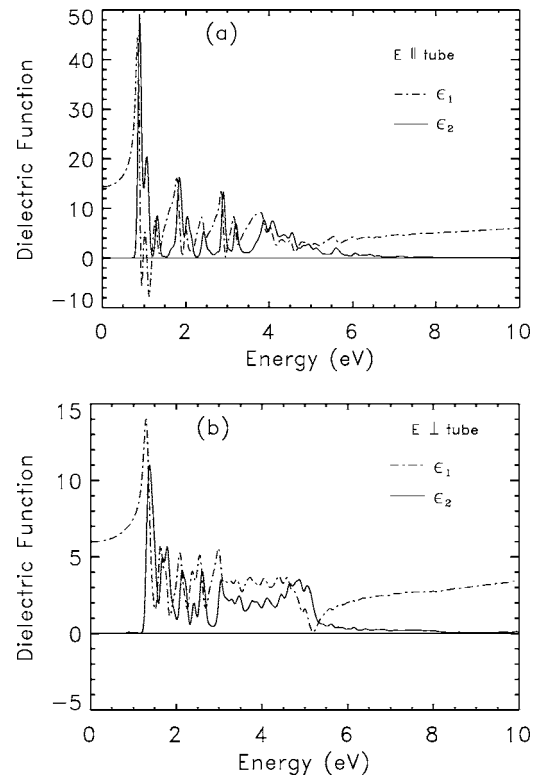


FIG. 7. The calculated real and imaginary parts of the dielectric function of the carbon nanotube (8,4) mat which has the tube-tube distance of 3.34 Å between the chiral SWCNTs (8, 4).

that of the carbon nanotube (16, 0) mat, which could indicate the effect of the nanotube curvature on the optical properties.

The calculated, strong anisotropy in the optical properties of the aligned carbon nanotube (10, 0) mat as well as the locations of the major absorption peaks in the imaginary part of the dielectric function ϵ_2 agree with those properties of the isolated or nearly isolated carbon nanotubes that were calculated by Guo *et al.* using supercells of a square array.¹¹ In this work, we are particularly interested in the aligned carbon nanotube mats that are constructed from semiconducting SWCNTs for optoelectronic applications. Guo *et al.* presented the calculated results of ϵ_1 and ϵ_2 for the isolated SWCNT (10, 0) (Fig. 8 in their article)¹¹ when the electric field is parallel and perpendicular to the nanotube axis. However, they did not present the magnitude of the first absorption peak in ϵ_2 when the electric field is parallel to the nanotube axis. The location of the first major peak in ϵ_2 for the electric field in parallel to the nanotube axis was found at about 0.75 eV from our calculation. This finding is in agreement with the result of Guo *et al.* of about 0.8 eV, estimated from their graph.

C. Single-walled carbon nanotube (8, 4) mat

The electronic structure of nonsymmorphic SWCNT (8, 4) has been studied by *ab initio* density functional calculations in previous work.^{16,26} The diameter of SWCNT (8, 4) is 8.29 Å. We constructed a carbon nanotube (8, 4) mat by arranging the SWCNTs (8, 4) in a triangular lattice. The tube-tube distance in the mat in the triangular lattice is 3.34 Å, as that in the carbon nanotube (10, 0) mat. We per-

formed *ab initio* density functional computations to study the optical properties of the carbon nanotube (8, 4) mat. Figure 7 presents the calculated optical properties, i.e., the real and imaginary parts of the dielectric functions as functions of the photon energy. Figures 7(a) and 7(b) present the cases of the electric field polarization of the light parallel and perpendicular to the tube axis, respectively. Similar to the carbon nanotube (16, 0) and (10, 0) mats, there is a strong peak in the imaginary part (ϵ_2) of the dielectric function near the absorption edge at about 0.89 eV, when the electric field of the light is parallel to the tube axis. The imaginary part (ϵ_2) of the dielectric function can reach a value of about 49 at the photon energy of 0.89 eV. There is a strong anisotropy in the optical properties in the carbon nanotube (8, 4) mat, as shown in Figs. 7(a) and 7(b).

IV. CONCLUSION

In this work, we studied the optical properties of the aligned carbon nanotube (16, 0), (10, 0), and (8, 4) mats for photonic device applications. We employed *ab initio* density functional computations to calculate the imaginary and real parts of the dielectric functions as functions of the photon energy. The calculated dielectric functions of the aligned carbon nanotube (16, 0), (10, 0), and (8, 4) mats present a strong anisotropy when the electric field of the light is parallel or perpendicular to the tube axes. Especially, there are strong peaks in the imaginary part of the dielectric function near the absorption edges, when the electric field of the light is parallel to the carbon nanotube axes. The unusual optical properties of the semiconducting carbon nanotube mats present an opportunity for applications in electro-optical devices in the infrared energy region.

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